

Direct Calculation of Liquid-Vapor Phase Equilibria from Transition Matrix Monte Carlo Simulations

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The phase behavior of real fluids and model systems is of significant interest to scientists and engineers. In this presentation, a novel approach for directly determining the liquid-vapor phase equilibrium of a model system at any temperature along the coexistence line is described. The method relies on transition matrix Monte Carlo ideas developed by Fitzgerald et al. During a simulation attempted transitions between states along the Markov chain are monitored as opposed to tracking the number of times the chain visits a given state as is done in conventional simulations. Data collection is highly efficient and very precise results are obtained. The method is implemented in both the grand canonical and isothermal-isobaric ensemble. The main result from a simulation conducted at a given temperature is a density probability distribution for a range of densities that includes both liquid and vapor states. Vapor pressures and coexisting densities are calculated in a straightforward manner from the probability distribution. The formalism described here also provides a means to calculate surface tensions. Liquid-vapor free energy barriers are extracted from the density probability distribution and the finite-size scaling method of Binder is used to determine infinite system surface tensions from finite system data. The new approach is demonstrated with the Lennard-Jones fluid and the SPC/E model for water. Coexistence properties, including surface tensions, for the Lennard-Jones system are directly calculated at temperatures spanning from the triple point to the critical point. Calculations for the SPC/E model are performed from temperatures of 300 to 600 K.